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Conductivity losses in ferroelectric phase of TGS

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Triglycine sulphate (TGS) is a crystal having a typical second order ferroelectric transition and the Curie point around 49 ^oC. It is quite easy to grow and to analyse its properties. Our TGS crystals were grown by slow solvent evaporation in paraelectric phase, around 54 ^oC, where no mechanical tensions due to ferroelectric domains were present. Dielectric properies of TGS crystals were continuously measured at a pace of 0.6 ^oC/min, starting from 65 ^oC, crossing down the Curie point until zero Celsius, on the frequency range $1\div10^7$ Hz. The two component of permittivity were measured and the parameters vs. temperature were estimated and analysed.

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1. Introduction

TGS ferroelectric crystals are still intensively studied on fundamental aspects and intesively used for technological applications, like sensitive pyroelectric devices, nonvolatile memories, storage devices and nanofabrication. Studies have been made on the relaxation phenomena of the ferroelectric domains [1-5], dielectric relaxation [6-9], lattice dynamics [10-12], ionic conduction and space charge polarization [13,14]. The crystal growing conditions of TGS in the paraelectric phase and and some other important properties have been already presented [15,16]. We shall analyse here the importance of conduction in the ferroelectric phase, down the Curie point until aproximately the room temperature.

2. Experimental

TGS crystals were grown in a thermostated oven at 54 ^oC, i.e. in paraelectric phase. The basic substance TGS was obtained from the components and refined by fractional recrystallization from solution [17]. Samples were obtained by clivage from single crystal, were polished and electrodes were obtained by silver painting.

The dielectric spectrometer Alpha-A Novocontrol was ued for mesurements on the teperature range from 65 ^oC until zero Celsius. The temperature was decreased according to the temperature program of spectrometer at a constant rate of 0.6 ^oC/min. The two components of permittivity were automatically measured and registered on the frequency range 1 Hz ÷ 10 MHz (further represented in log scale).

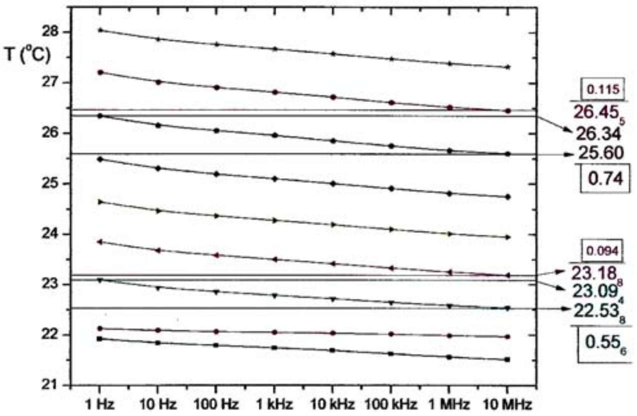


Fig. 1. The temperature variation during succesive sets of frequency measurements.Theirs variation during taking a set is between 0.74 ^oC and 0.56 ^oC, or less

Five equidistant measuring points were registered on every decade of the frequency range. Some data are presented in Fig. 1. Thus, one set of frequencies measurements on $1\div10^7$ Hz, was taken in aproximately one minute, while. the temperature decrease was ~ 0.6 ^oC.

3. Results

According to the Debye concept, taking into consideration the conductivity of the sample, we have:

$$\varepsilon' = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+\omega^2\tau_\varepsilon^2} \tag{1}$$

$$\varepsilon'' = \frac{\omega\,\tau_\varepsilon(\Delta\varepsilon)}{1+\omega^2\tau_\varepsilon^2} + \frac{\sigma}{\varepsilon_o\omega} \qquad (2)$$

where $\Delta\varepsilon = (\varepsilon_{st} - \varepsilon_\infty)$ the dielectric strength is the diference between the extreme values of permittivity (vs. frequency), σ is the conductivity, ω is the angular velocity and τ_ε the relaxation time. The last term in eq. 2 represent the a.c. conductivity losses $\Delta\varepsilon''_{cond} = \sigma/\varepsilon_o\omega$ which theoreticaly has a reverse dependence on the angular velocity. In fact, experimentaly this dependence was found $\Delta\varepsilon''_{cond} \sim \omega^{-N}$ and it has a specific frequency and temperature dependence. N coefficient is smaller than one, showing a week frequency dependence.

In our case, as previously shown [8, 9], there are 3 relaxation processes, at LOW (L), MIDDLE (M) and HIGH (H) frequency and the distributions are of the Cole-Cole type [18]. The conduction component estimation was made with the program of the spectrometer.

The frequency distribution of the dielectric components are presented in Fig. 2, as an example, at the temperature 48.2 °C. Here, the losses component represent 45%, 5.2% and 0.2% from the basic measured value of the imaginary component of dielectric at the frequencies 10^2, 1.6 10^4 si 5.5 10^5 Hz respectively, corresponding to L, M and H components. At the lower limit of frequency of 1 Hz the losses component exceed 98%.

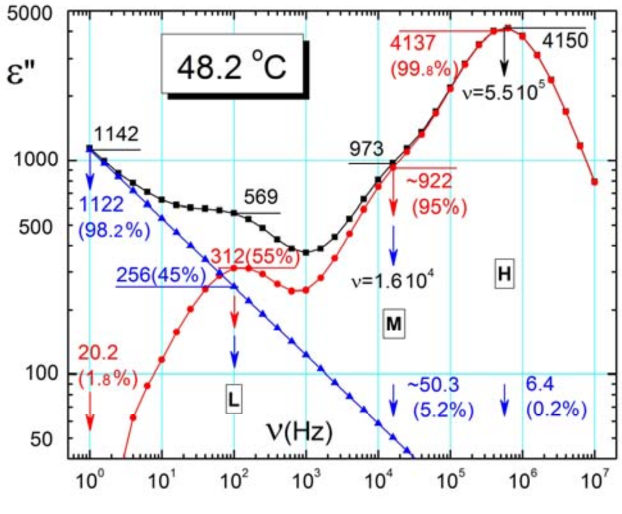
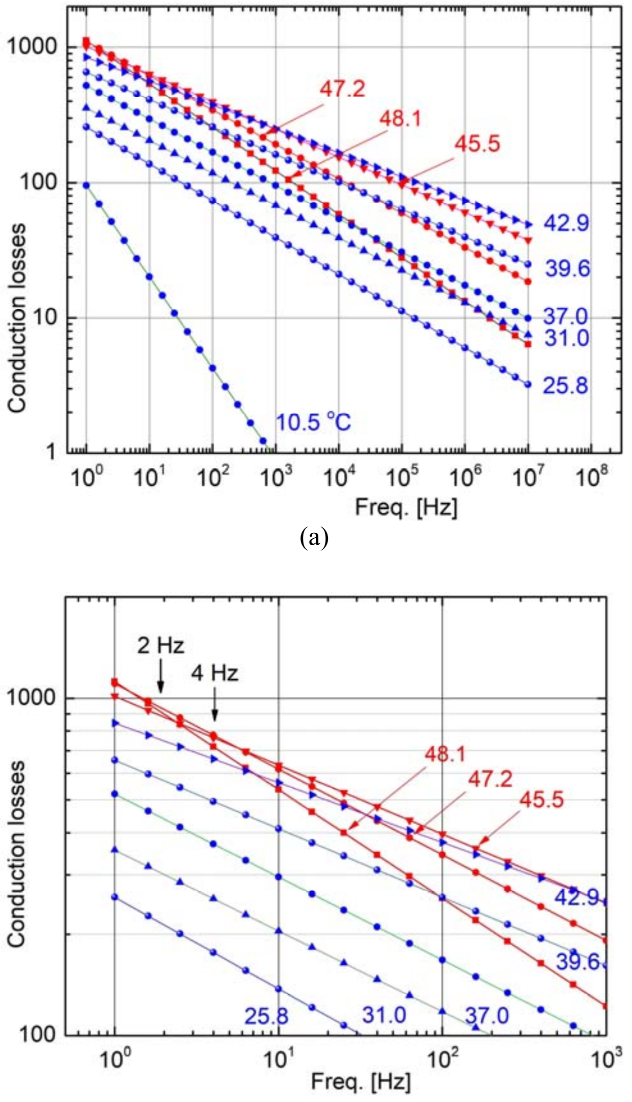


Fig. 2. Estimation of conduction component vs. frequency at 48.2 °C (double log scale)

The temperature dependence of conductivity component $\Delta\varepsilon''_{cond}$ in Fig. 3 (a), 3 (b) shows a conspicuos temperature dependence. The components do not have a monotonous temperature (parametric) dependence. Down the Curie point, the slope N of the liner frequency dependence of losses (in double log scale), rapidely decreases until ~ 45°C and appear to have a congruent point somewhere between 2 and 4 Hz (see Fig. 3 (b)).



(a)

(b)

Fig. 3. (a) Conduction losses $\Delta\varepsilon_{cond}$ vs frequencies, at several temperatures in the ferroelectric phase; (b) Detail from Fig. 3 (a)

At temperatures around 45 °C the slope N has a turning point (see Figs. 3 and 4). Down the temperature of 45 °C, N start to increase again and the linear intercept (at ν =1 Hz) monotonously decreases. This dependence is valid until about 25 °C, where the transition can be considered already finished. Down to this temperature, until zero Celsius, the dependence has no longer a regular and stable caracter (see Fig. 3 (a)).

4. Conductivity

Conductivity spectra and the dielectric constant present the same physical information, because they are simple corelated [20], by the equation:

$$\sigma^*(\omega) = i\,\omega\,\varepsilon_o\,\varepsilon^*(\omega) \qquad (3)$$

Eq. 3 can be writen:

$$\sigma' + i\,\sigma'' = i\,\omega\,\varepsilon_o\,[\varepsilon' - i\varepsilon''] = \omega\,\varepsilon_o\,\varepsilon'' + i\,\omega\,\varepsilon_o\,\varepsilon' \qquad (4)$$

In our case the conductivity was estimated from the equation:

$$\sigma = \sigma' = \omega\,\varepsilon_o\,\varepsilon'' = \omega\,\varepsilon_o\,\Delta\varepsilon''|_{\nu\text{-}1\,\mathrm{Hz}} \qquad (5)$$

The conduction losses component $\Delta\varepsilon''_{cond}$ considered at the frequency of 1 Hz, in Fig. 2, represent more than 98% of the experimentally measured value. This means the second term in eq. (2) prevails over the first one.

The conductivity at the frequency of 1 Hz was calculated with the computer, using eq.(6) at several temperatures. Data are presented in Arrhenius coordinate in Fig. 4.

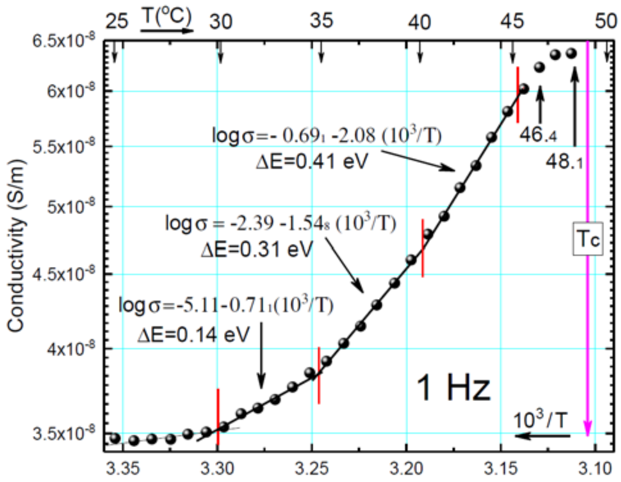


Fig. 4. Conductivity vs temperature in Arrhenius coordinate. Activation energy is shown on several temperature interval. Strange, nonlinear behaviour of conductivity appears on the interval Tc → 46.4 °C. Note, the abscisa scale was reversed

Table 1. Activation energy of conductivity on several temperature intervals in ferro phase, Fig. 4

Temperature (°C)	Tc – 45	45 - 40	40 - 35	35 - 20
ΔE (eV)	....	0.41	0.31	0.14

Careful fitting of conductivity vs temperature, shows a defined number of zone having linear temperature dependence, as in Fig 4. Roughly, the slope of these dependences decreases with temperature. The slope changes of this linear conductivities take place approximately at temperatures: 45 °C, 40 °C 35 °C, 30 °C.

This temperatures are very close, or coincide with the temperature points, where slope changes take place for other parameters of TGS analysed in ref. [9] (see Figs. 3b, 5b, 5c, 7, 9).

The temperature dependence of conductivity represented as:

$$\sigma = \sigma_o \exp(-\,\Delta E/\,k_B T) \qquad (6)$$

shows the activation energy (ΔE) presented in Fig. 4 and in Table 1, on several temperature intervals. The estimated values of these activation energies, agree very well with the value 0.34 eV found in ref. [29]. On the other hand, the literature values of conductivity, of about 2.5-8.3 [21], [22] and 1-6 [29] fall on the conductivity range we have estimated in Fig. 4 (see also the data in Table 3).

5. Temperature dependence of ”N”, the frequency coefficient

As seen in Fig. 3, the distribution of conduction losses components has a frequency dependence in the ferroelectric phase:

$$\Delta\varepsilon''_{cond} \sim \omega^{-N} \qquad (7)$$

where N –the frequency coefficient is smaller than one.

Accordding to Eq. 7, N is the slope in equation of conductivity components vs frequency in double log scale. The estimated values of N are presented versus temperature, in Fig. 5. Here, around 45 °C there is a ”strange” turning point of N values versus temperature (see also Fig. 3). The characteristic data are collected in Table 2.

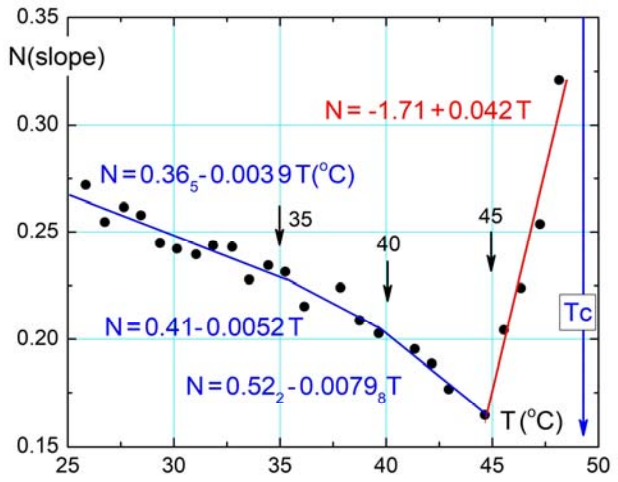


Fig. 5. The temperature dependence of the slope N of permittivity conduction losses vs frequency, Fig. 3

Table 2. The slope (N coefficient) and the intercept, on several temperature intervals in Fig. 4

Temperature (^oC)	Tc ÷ 45	45 - 40	40 - 35	35 - 25
Inteercept	- 1.71	0.52_2	0.41	0.36_5
N = Slope $(deg\ C)^{-1}$	0.042	-0.0079_8	- 0.0052	- 0.0039

Crossing down the Curie point, N coefficient substantialy decreases 0.32 ⇒ 0.16 on the temperature range Tc ⇒ 45 ^oC, i.e. slope dN/dT = 0.o4 K^{-1}. Than, the coefficient increses with the temperature decrese, having slope changes in steps around 45, 40 and 35 ^oC. On the whole temperature range 45 ⇒ 25 ^oC, the mean value of dN/dT = - 0.0055 K^{-1}, i.e. almost one order of magnitude smaller than the previous slope and of opposite sign (see Table 2).

This abnormal behaviour, correlated with some other similar aspects were analysed in refs. [3] (Figs. 8-10) and [19] (Figs. 4-6). The temperature region of about 3-4 ^oC down the Curie point appears as an ”instability” zone.

6. Discussions I

The program of experimental measurements was so adjusted, data to be continuously registered on 35 selected frenquencies (5 on every decade), on the range $1 \div 10^7$ Hz during the slow temperature decrease (see Fig. 1 as an example). At a pace of 0.6 ^oC/min temperature decrease, measurements were made in only 5/6 minutes from Tc to 45/46 ^oC; in 15 min. until 40 ^oC and in 25 min. until 35 ^oC, where the ferro transition effect is definetly closed [9]. This way, the first stages of metastable state evolution of electrical parameters, in the ferroelectric phase of TGS was registered.

Table 3. Conductivity and activation energy of TGS, KDP and DTGS in several conditions, from literature data. References [23]-[28] shows D.C. conductivities. Relevant A.C conductivity data are from references [21], [22] and [29]

Authors	σ (S/m)	(conditions)	ΔE - activ energy (ferro / para phase)
[21] E.T.Keve et al 1972	$(2.5\text{-}8.3)\cdot 10^{-8}$	(20°C, 1.6 kHz)	-------
[22] K.L.Bye et al 1972	$8.3\cdot 10^{-8}$	(21°C, 1.6 kHz)	-------
[23] F.Moravec et al 1969	10^{-11}	(~ 47°C, humid <5%)	1.7 / 0.7 eV
[24] B.Hilczer et al 1978	$\sim 5\cdot 10^{-10}$	(close Tc, guard ring) rejuvenated (80°C/110 h)	1.79 / 097 eV 1.41 / 0.43 eV
[25] A. Saxena et al 2005 [26] A.Saxena et al 2001	$2.3\cdot 10^{-11}$ $4.3\cdot 10^{-11}$	(27 °C) (69 °C)	1.36 / 0.74 eV
[27] C.Ray et al 2011	$5.5\cdot 10^{-11}$	(35°C)	1.42 / 0.71 eV
[28] Batra et al 1985	$1.45\ 10^{-10}$ $4.68\ 10^{-10}$	(300 K) (near Tc)	------- -------
[29] P.R.Deepthi et al 2016	$1\text{-}6\cdot 10^{-8}$	(300 K)	0.34 / --- eV
[30] E.D.Yakushkin et al 2001	$10^{-9} \div 10^{-5}$	(KDP crystal several sections)	0.3 ÷ 1 eV
[31] A.V.Shil’nikov et al 1999	$7\cdot 10^{-9}$ $1.5\cdot 10^{-8}$	(DTGS, 1 Hz, Tc-2°C) (DTGS, 10 Hz, Tc-2°C)	--- / 0.94 eV

In Table 3, we have collected literature data of conduction and activation energy for TGS and for KDP and DTGS, to compare with. There is a large spectrum of published data values, measured in D.C. and A.C. at several temperature [32]-[36].

The A.C. conductivity measured for TGS at usual frequencies are about of the order $\sim 5\times 10^{-8}$ S/m, see the refs [21],[22], [29] and even data for DTGS [31] at low frequencies are comparable with the data we have estimated (see Fig. 5 and Table 2).

In fact, generally, the measured conduction data cover two type of conductivity:

$$\sigma = \sigma_{DC} + \sigma_{AC} = \sigma_{DC} + A\,\omega^N \qquad (8)$$

Here, σ_{DC} - the DC conductivty values are about two order of magnitude lower than σ_{AC} - the AC conductivity (see Table 3). Thus, only the second term in eq. (6), which is frequency dependent has been measured, like in refs [32-36].

Our data, presented in Fig. 4 are comparable with the data of Keve and Bye [21], [22], the data of Deepthi et al [29] and similar to the data measured for DTGS [31]. Besides, we have found the temperature dependence of conductivity on several domain, in ferro phase. This facts might be correlated with the metastable phase evolution in the first stages, we have registered during measurements (domain and lattice dynamics might be involved).

7. Discussions II

In order to check the temperature dependence of conductivities in the ferroelectic phase, the data for deuterated TGS (DTGS), from ref. [31] were further analysed.

Conductivities for 1 Hz and for 10 Hz, drawn from ref. [31] are represented in Figs. 6 and 7, in Arrhenius coordinate.

Activation energy for both frequencies are presented in Table 4. The estimated values are larger than the values for pure TGS in the ferroelectric phase, but the stages in the temperature dependence of conductivitiy appear clearly.

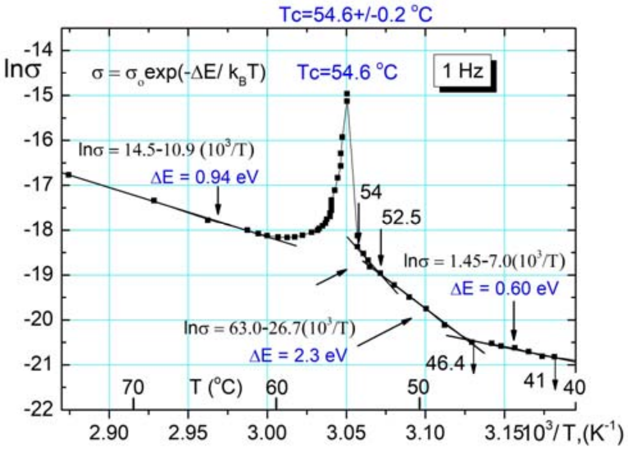


Fig. 6. Conductivity and activation energy for DTGS at 1 Hz. Data estimated using experimental data from ref. [31]

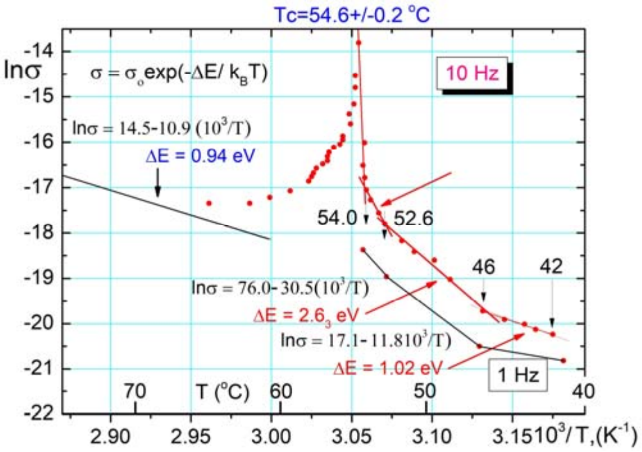


Fig. 7. Conductivity and activation energy for DTGS at 10 Hz. Data estimated using experimental data from ref [31]

Table 4. Activation energy of conductivity in DTGS from Fig. 6 and Fig. 8 on several temperature interval estimated from ref. [31]

Temperature (^{o}C)	80^{o}C - Tc	52.5 - 46.2	46.2 – 41.5
ΔE (eV) - 1 Hz (Fig. 8)	0.94	2.3	0.60
ΔE (eV) - 10 Hz (Fig. 9)	-----	2.6	1.02

The activation energy in the temperature range 54-52.5 ^{o}C, was estimated as 3.6 and 5.5 eV for 1 Hz and 10 Hz respectively, might not be valed, being in the zone of instability of about 4 ^{o}C down the Curie point (see Fig. 4). These estimated conduction data for DTGS in ferroelectric phase confirm that the activation energy, like for TGS, has specific values on some temperature intervals.

On the other hand, the higher values of the activation energy for DTGS vs TGS in the lower temperature ranges suggest the hydrogen/deuterium atom are realy involved in the AC conduction.

8. Conclusions

Dielectric components of TGS crystal were measured with the dielectric spectrometer Alpha-A Novocontrol, decreasing temperature from 65^{o}C, crossing down the Curie point until zero Celsius, on the frequency range $1 \div 10^7$ Hz. Conductivity was estimated from the imaginary component of permitivity with the program of the spectrometer.

Conduction losses vs frequency (in double log scale) shows an instability on the range of 3-4 ^{o}C down the Curie point in Fig. 3 (a) and (b). The frequencies coeficient N (in eq. 3) confirm this instability, having a higher reversed slope vs temperature, 4 ^{o}C down the Curie point, until about 45 ^{o}C (see Fig. 5).

First stages of the metastable state of conduction losses measured in the ferroelectric phase (fig 4), shows a sequential slope decrease vs temperature down the Curie point. The slope changes take place at temperature 45, 40, 35, 30 ^{o}C, similar to other TGS parametrs analysed in ref. [9] (Figs. 3 (b), 5 (b), 5 (c), 7 and 9). The conduction losses we have measured for TGS, are of the same order of magnitude (~10^{-8} S/m) as presented in refs. [21, 22, 29] and about of the same order of magnitude of the activation energy.

Conductivities data published in ref. [31] for DTGS, we have analysed down the Curie point (Tc=54.6 ^{o}C), in the ferroelectric phase for the two frequencies 1 and 10 Hz. Estimated conductivities changes also secventially in ferro phase and is about of the same order of magnitude as for TGS. However, the activation energy for DTGS is higher (compare the data in Table 4 and Table 2), sugesting the jump of deuteron (and protons for TGS) are involved in the conduction mechanism.

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